Skeletal Concentrations of Lead, Cadmium, Zinc, and Silver in Ancient North American Pecos Indians

by Jonathon E. Ericson,* Donald R. Smith,† and A. Russell Flegal‡

Bone samples of 14 prehistoric North American Pecos Indians from circa 1400 a.d. were analyzed for lead, cadmium, zinc, and silver by graphite furnace atomic absorption spectrometry to establish the baseline levels of these elements in an ancient North American population. Measurements of outer and inner bone fractions indicate the former were contaminated postmortem for lead, zinc, and cadmium. The contamination-adjusted average ($\hat{x} \pm SD$) level of lead (expressed as the ratio of atomic lead to atomic calcium) in bones of the Indians was $8.4 \pm 4.4 \times 10^{-7}$, which was similar to ratios in bones of ancient Peruvians (0.9 to 7.7 × 10⁻⁷) and significantly lower than ratios in bones of modern adults in England and the United States (210 to 350×10^{-7}). The adjusted average concentrations (microgram per gram dry weight) of biologic cadmium, silver, and zinc in the Pecos Indian bones were 0.032 ± 0.013, 0.094 ± 0.044, and 130 ± 66, as compared to concentrations of 1.8, 0.01 to 0.44, and 75 to 170 in the bones of modern people, respectively. Therefore, cadmium concentrations in Pecos Indian bones are also approximately 50-fold lower than those of contemporary humans. These data support earlier findings that most previously reported natural concentrations of lead in human tissues are erroneously high and indicate that natural concentrations of cadmium are also between one and two orders of magnitude lower than contemporary concentrations.

Introduction

Human exposure to anthropogenic lead in the Old World dates back over 4500 years to the inception of cupellation (refining of precious metals by fire) and has increased nearly exponentially since that time (1,2). Therefore, ancient human remains from Old World regions and subsequent to circa 2000 to 3000 B.C. should not be used to determine the natural body-levels of lead (3). The northern hemisphere of the New World has also been impacted by aerosol transmission of anthropogenic lead during that period (4,5) due to a predominant latitudinal tropospheric distribution of lead aerosols (6), as well as from industrial uses of lead within the New World. An approximate 500-fold increase in contemporary human skeletal lead burdens was revealed in a previous study (3), which used development of ultra-clean techniques (7). In that study, Ericson et al. (3) determined the skeletal lead burden (Pb/Ca atomic-corrected) of ancient Peruvians (1600 years before present) to be 0.3×10^{-7} , compared to 210 to 350 $\times 10^{-7}$ found in contemporary humans of the industrialized northern hemisphere (8–14). That increase is due to massive global atmospheric emissions of anthropogenic lead, which are currently estimated at 3×10^8 kg/yr (15). Other studies (16–19) have reported smaller historical increases in skeletal lead, though their results may be qualified by concerns of contamination, since they did not employ ultra-clean analytical techniques.

Several processes have been suggested to account for differences in lead concentrations of buried ancient bones. It has been suggested that biologic lead is leached out of buried bone, thereby diminishing lead concentrations with increased burial time (20). Proponents of that process believe that lead levels in ancient skeletal remains underestimate true natural levels. which supposedly were much higher, and that lead levels in bones of contemporary humans are natural and normal. Conversely, it has also been suggested that low lead concentrations in ancient remains reflect very low levels in an unperturbed, natural environment and that lead levels in those buried bones may have been elevated by subsequent exposure to natural soil lead and industrial lead (3,21). The latter process, which we believe is more accurate, indicates that natural lead levels

^{*}Program in Social Ecology, University of California, Irvine, CA 92717.

[†]Department of Biology, University of California, Santa Cruz, CA 95064.

[‡]Institute of Marine Sciences, University of California, Santa Cruz,

Address reprint requests to J. E. Ericson, Program in Social Ecology, University of California, Irvine, CA 92717.

ERICSON ET AL.

of ancient humans may be overestimated in analyses of buried remains, and those analyses must be corrected to accurately establish natural lead concentrations. Consequently, the very high skeletal lead concentrations (subclinical) in contemporary humans are in extreme excess (two to three orders of magnitude) of natural levels due to exposure and accumulation of ubiquitous industrial leads.

Skeletal remains of North American Pecos Indians buried in arid desert soils were studied to compare ancient human lead levels between different hemispheres of the New World and to establish the preindustrial baseline levels of cadmium, zinc, and silver in human bone tissue. The skeletal remains recovered from Pecos Pueblo, New Mexico, compose one of the largest and stratigraphically best-documented collections of human osteological material in the New World (22). This allowed for careful selection of samples that were well suited (i.e., adequate size, physical integrity, and representative of the population) for characterization of skeletal trace metal levels by ultra-clean elemental analysis. These four trace metals were chosen because the magnitudes of their emissions from industrial sources are high relative to those from natural processes, they have no biological function with the exception of zinc, and they exhibit some level of toxicity to humans (23-25).

Lead, zinc, cadmium, and silver are accumulated in bone to different degrees and for different reasons. Lead is a biogeochemical analog to calcium (3,26,27), though it has no known biologic role and is only present as a contaminant in the body. Seventy to 95% of a vertebrate's body lead burden is contained within the skeleton (12), where it is associated with the mineral matrix (28,29). Zinc is ubiquitous in body tissues and serves many essential functions in numerous protein and enzyme systems (30). Approximately 28% of the body's zinc is localized in bones and teeth (31), where it is largely (98%) mineral associated (28). Cadmium, like lead, serves no biological function and is virtually absent from humans at birth (32). Over 50% of the body cadmium burden is localized in the kidneys and liver, while comparatively little accumulates in bones (24,33,34). However, the large relative contribution of osseous tissue to total body mass suggests bones may contain a notable fraction of body cadmium burdens. Silver is also a nonessential element in organisms and is apparently poorly accumulated under normal physiological conditions (35). As with cadmium, it is most commonly associated with a low molecular weight metallothionein protein pool in liver and kidney tissues (23,36).

Lead and its biochemical analog calcium were measured to determine the validity of the conclusions of Ericson et al. (3) on a global scale. Specifically, it was unknown whether the historical 500-fold increase of lead indicated by their data was partially due to hemispheric differences in the human uptake of natural lead. Silver was measured because its historical increase in anthropogenic emissions has paralleled that of lead, since the latter was initially emitted as an industrial waste prod-

uct in the production of silver from the cupellation of argentiferous galena (1,37). Zinc also has a long history (> 2000 years) of anthropogenic emissions as a major alloying ingredient in the production of brass (38). Its industrial production has paralleled that of cadmium, which is a biogeochemical analog of zinc and is characteristically present as a trace constituent in zinc sulfide deposits. Therefore, the following ultra-clean measurements of ancient human skeletal lead, cadmium, zinc, and silver concentrations provide quantification of the industrial perturbations of those elements in the biosphere.

Materials and Methods

Sample Selection

Fourteen human bone samples (Table 1) were selected from the Harvard University Peabody Museum's extensive collection of over 900 Pecos Indians (39,40). Selection criteria were based on physical size (i.e., large enough to render a relatively pristine inner bone subsample) and overall integrity. This excluded highly fractured bones and those showing evidence of excessive diagenetic alteration (physiochemical changes that occurred within the bone during and after burial in sediments). Classifications based on osteological analyses by Hooten (39) and Ruff (22,40) were used to select bones of different anatomical origin, gender, and age groups to represent the population with a relatively few number of samples. This introduced additional sources of variance, since skeletal lead levels are known to vary with bone type (cortical versus trabecular) and age of the individual (41). Differences in bone lead levels between males and females have also been demonstrated, though these have been largely attributed to varying degrees of exposure between the two groups (41,42).

The human burials were excavated by A. V. Kidder at Pecos Pueblo, beginning in 1915, and continued intermittently until 1925 (43). Pecos Pueblo was occupied

Table 1. Archaeological data on Pecos Indian bones collected from Pecos Pueblo, New Mexico.

Analytical sample no.	Peabody no.	Bone*	Gender ^b	Age atdeath, years
1	60078	P	?	4-6
2	60206	Т	?	6
3	60079	P	?	6
4	60151	P	?	8
5	60023	P	M	18
6	60107	T	F	19
7	60685	P	?	22 - 23
8	59924	P	M	28
9	60285	0	\mathbf{F}	34
10	60695	\mathbf{F}	M	39
11	60180	0	M	40 - 49
12	60602	PT	M	40 - 49
13	60562	0	M	50 +
14	60216	P	\mathbf{F}	50 +

^aP, parietal; T, temporal; O, occipital; F, frontal; PT, parietal temporal.

bM, male; F, female; ?, unknown.

from 1300 to 1823 A.D. and is located in north central New Mexico (35° 34′N, 105° 37′W) (43). Samples were of individuals buried at Pecos Pueblo in association with architectural features and temporally diagnostic glazed ceramic wares. Six glaze types (44) were dated by the dendrochronology of that region (43). The Pecos Pueblo appears to have been settled by sedentary agriculturalists (43), whose diet would have included maize, beans, squash, and sunflower seeds (45), in addition to wild animals hunted in the nearby mountains and plains to the east (46).

While the people of Pecos Pueblo lived in a relatively pristine environment, they still may have been exposed to some anthropogenic lead from lead glaze-painted ceramics. They produced lead glaze-paint ceramics for decorative purposes, beginning during Glaze Ware III and continuing to Glaze Ware VI (47). Production of glaze wares supplied only local use, since with few exceptions, they were not exported. Raw materials for the lead glass glaze contained varying amounts of iron and manganese (47) and were obtained from the people at Galisteo who controlled the cerussite (lead carbonate) source associated with turquoise in the Ortiz Mountains to the southwest of Pecos Pueblo. This may have contributed to some of the variation among individuals in the following bone lead concentrations, and the lead concentrations of all those individuals are considered to be elevated compared to those preindustrial individuals with no industrial lead exposure.

Sample Preparation and Analysis

The samples were processed in a Class-100 trace metal clean laboratory which meets the criteria established by Patterson and Settle (7). All commercial high purity acids were redistilled twice in subboiling quartz stills and only ultra-pure (18 megaohm) water was used. All containers were acid-cleaned and preconditioned with the ultra-pure reagents used in the digestion. Individual and procedural blanks were processed and measured concurrently. The analyses were intercalibrated with concurrent analyses of National Institute of Standards and Technology (NIST) standard reference material (SRM 1577a).

A set of inner and near-surface outer bone was obtained from each of the fourteen bone fragments. Inner, compact bone samples were obtained by grinding away exterior cortical surfaces with an acid-cleaned (concentrated HNO₃) drill bit. The resulting samples were repeatedly rinsed with dilute nitric acid and ultra-pure water to minimize contamination of the inner bone with outer bone fragments created from the drilling process. This cleaning procedure does not preferentially remove lead relative to calcium (3). Any potential contribution of the drill bit to the lead content of the samples, either directly or through forcing microparticles of the external cortical surface into interior microfractures, appeared to be minimal, based on microscopic analyses.

The companion outer bone samples consisted of cortical and cancellous bone fragments created during the

drilling process. These were prepared concurrently with the inner bone samples to indicate the degree of surface contamination of the initial bone fragment. Neither of these samples included the outermost surface material, which was assumed to be heavily contaminated. This procedure eliminated diagenetically altered material, which results in postmortem addition of contaminant lead (and other trace elements) to bone surfaces during burial. It also allowed us to determine whether lead and other elements were leached from bone surfaces, or if those elements were added to bone as contamination from the soil during burial.

Bone samples ranging from 0.1 to 2.4 g (dry weight) were digested in quartz beakers with concentrated nitric and hydrochloric acids. Analyses were conducted on a Perkin-Elmer model 603 atomic absorption spectrometer equipped with a deuterium arc background corrector, HGA 500 graphite furnace, and AS 40 autosampler. Samples were analyzed using the method of standard additions with replicate sample injections.

Our data are presented on a bone dry weight basis and normalized to bone calcium content. Skeletal trace element concentrations presented only on a wet or dry weight basis introduce analytical error, in addition to confounding comparisons between samples, due to substantial differences in both mineral and nonmineral content between bone types and individuals sampled (41).

Results

Concentrations and Atomic Ratios

Elevated lead, zinc, and cadmium levels of the outer relative to inner bone fractions indicate that the outer fractions are contaminated (Tables 2 and 3). This is most apparent with lead in outer bone, which is 2- to 10-fold higher than in inner bone. These concentration and atomic ratio gradients indicate that outer bone contains both metabolic lead and contaminant lead incorporated after death. The latter may include a) soil lead added by diagenetic processes (3) and b) industrial lead added during collection, storage, and handling activities (48). These gradients are analogous to those in ancient ice cores (49), which resulted from the intrusion of contaminant lead through minute cleavages in the ice matrices. Smaller elevations (50%) of zinc in outer bone exhibit similar parallels, while cadmium decreases from outer to inner bone in about half of the samples, and the remaining 50% show either no change or a small increase in inner bone. The latter may be due to loss of cadmium in bone proteins during biodegradation. These trends are consistent with the postmortem contamination of buried ancient remains, and evidence diagenetic alteration of these elements in the bones. Conversely, silver levels typically increase from outer to inner bone, suggesting that silver was leached from bone surfaces during burial. Although it is possible that natural gradients between inner and outer bone are due to differential metabolic incorporation and/or resorption of these four elements, it is most likely that these gradients result

ERICSON ET AL.

Table 2. Elemental concentrations of Pecos Indian bones."

Analytical	Ele	mental cor	acentration	ıs, μg/g dr	y weight
sample no.	Pb	Ag	Cd	Zn	Ca, %
1 (i)	0.68	0.039	0.19	120.0	16.0
(0)	1.9	0.017	0.054	67.0	5.4
2 (i)	0.12	0.055	0.051	83.0	15.0
(0)	1.4	0.064	0.083	190.0	15.0
3 (i)	4.8	0.13	0.13	110.0	13.0
(o)	14.0	0.088	0.19	130.0	13.0
4 (i)	ND^b	0.10	0.024	62.0	13.0
(0)	3.5	0.23	0.031	110.0	17.0
5 (i)	0.58	0.075	0.21	140.0	18.0
(0)	1.4	0.052	0.14	250.0	17.0
6 (i)	2.0	0.078	0.36	240.0	16.0
(o)	1.8	0.019	0.41	280.0	9.4
7 (i)	1.1	0.070	0.22	260.0	16.0
(o)	5.1	0.12	0.17	250.0	17.0
8 (i)	1.9	0.16	0.036	94.0	12.0
(o)	6.9	0.12	0.057	150.0	18.0
9 (i)	0.28	0.56	0.033	110.0	17.0
(o)	0.80	0.44	0.15	110.0	15.0
10 (i)	0.78	0.066	0.035	84.0	13.0
(o)	4.0	0.061	0.021	130.0	16.0
11 (i)	0.89	0.077	0.036	210.0	13.0
(o)	12.0	0.083	0.13	380.0	16.0
12 (i)	1.8	0.092	0.27	450.0	13.0
(o)	14.0	0.14	0.73	680.0	14.0
13 (i)	0.78	0.41	0.008	75.0	16.0
(o)	7.4	0.13	0.048	290.0	50.0
14 (i)	3.5	0.19	0.088	82.0	14.0
(o)	6.1	0.10	0.091	110.0	11.0

^aInner (i) and outer (o) fractions analyzed per bone sample.
^bND, not detected (Pb concentration < 0.023 μg/g dry weight).

from the addition/removal of elements to outer bone postmortem. Consequently, data from the outer bone samples are considered to be invalid.

Concentrations and metal/calcium atomic ratios of all four trace elements in the inner bone samples varied by nearly an order of magnitude or more between the highest and lowest values. No correlates exist with gender or age of the individuals at death (Tables 1, 2, and 3).

Lead. Lead concentrations of inner bone range from below the analytical detection limit (< 0.023) to 4.8 μ g/g, and average ($\bar{x} \pm SD$) 1.5 \pm 1.4 μ g/g. Inner bone lead/calcium ratios parallel trends in concentrations and range from 1.6 \times 10⁻⁷ to 73 \times 10⁻⁷, with an average of 21 \pm 21 \times 10⁻⁷.

Cadmium. Cadmium concentrations of inner bone vary from 0.008 to 0.36 μ g/g and average 0.12 \pm 0.11 μ g/g. Cadmium/calcium ratios in inner bone range from 0.19 to 8.1×10^{-7} , and average $2.9 \pm 2.6 \times 10^{-7}$.

Zinc. Inner bone zinc concentrations (62 to 450 μ g/g) average 150 \pm 110 μ g/g, while zinc/calcium ratios in inner bone (2.9 to 21 \times 10⁻⁴) average 6.5 \pm 4.9 \times 10⁻⁴. Relative decreases of zinc and cadmium concentrations of individual bones are parallel, which is consistent with similarities in their natural and anthropogenic cycles.

Silver. Silver concentrations of inner bone range

Table 3, Metal/calcium ratios (atomic) of Pecos Indian bones.^a

Analytical sample no.	Pb/Ca, ×10 ⁻⁷	Ag/Ca, ×10 ⁻⁷	Cd/Ca, × 10 ⁻⁷	Zn/Ca, × 10-
1 (i) (o)	8.5 67.0	0.94 1.2	4.4 3.5	4.6 7.6
2 (i) (o)	1.6 18.0	1.4 1.6	$\begin{array}{c} 1.2 \\ 2.0 \end{array}$	$\frac{3.4}{7.8}$
3 (i) (o)	$73.0 \\ 220.0$	$\frac{3.9}{2.5}$	$\frac{3.6}{5.3}$	$\frac{5.3}{6.2}$
4 (i) (o)	ND ⁶ 40.0	$\frac{3.0}{5.2}$	0.68 0.67	$\frac{3.0}{3.9}$
5 (i) (o)	6.4 17.0	$\frac{1.6}{1.2}$	4.4 3.1	4.9 9.2
6 (i) (o)	24.0 36.0	1.8 0.75	8.1 16.0	$\frac{9.2}{18.0}$
7 (i) (o)	13.0 58.0	$\begin{array}{c} 1.7 \\ 2.6 \end{array}$	$\frac{5.0}{3.7}$	$\frac{10.0}{9.2}$
8 (i) (o)	30.0 74.0	5.0 2.4	1.1 1.1	$\frac{4.8}{5.1}$
9 (i) (o)	$\begin{array}{c} 3.2 \\ 11.0 \end{array}$	12.0 11.0	0. 6 9 3.6	4.1 4.6
10 (i) (o)	$\frac{12.0}{47.0}$	$\frac{2.0}{1.4}$	$0.98 \\ 0.48$	4.1 5.1
11 (i) (o)	$13.0 \\ 150.0$	2.2 2.0	$\frac{1.0}{2.9}$	9.9 15.0
12 (i) (o)	$\begin{array}{c} 27.0 \\ 190.0 \end{array}$	2.7 3.7	7.4 19.0	$\frac{21.0}{30.0}$
13 (i) (o)	$\frac{9.6}{29.0}$	9.6 0.95	0.19 0.34	$\frac{2.9}{3.6}$
14 (i) (o)	50.0 110.0	5.0 3.7	2.3 3.1	3.6 6.5

[&]quot;Inner (i) and outer (o) fractions analyzed per bone sample.

^bND, not detected (Pb concentration $\leq 0.023 \mu g/g$ dry weight).

from 0.039 to 0.56 µg/g and average 0.15 \pm 0.15 µg/g, while silver/calcium ratios (0.94 to 12 \times 10⁻⁷) average 3.8 \pm 3.3 \times 10⁻⁷.

Estimates of Natural Concentrations

Since metal concentration gradients between inner and outer bone fractions indicate that outer bone trace element levels have been altered (contaminated) postmortem, inner bone values may be similarly qualified by concerns of contamination. Some of those inner bone concentrations and atomic ratios appear to be anomalously high and would therefore positively bias our estimates. We identified these samples for exclusion by employing the metal/calcium ratios as a measure of an anomalous increase in (contaminant) metal levels. For example, if an inner bone metal/calcium ratio was greater by an arbitrary factor of 10 or more than the lowest measured ratio for that metal (one nondetected value for lead was not considered), the sample was considered to be excessively contaminated. This procedure identified values for lead in sample numbers 3, 6, 8, 12, and 14; cadmium in sample numbers 1, 3, 5, 6, 7, 12, and 14; silver in sample numbers 9 and 13; and zinc in sample number 12. The anomalously high values in those inner bone samples typically correspond with higher values in the companion outer bone samples, which evidences an external source of contamination. Exceptions to this feature do exist (e.g., cadmium sample numbers 1, 5, and 7, and silver sample numbers 9 and 13), though explanations for these are unclear.

Contamination-adjusted averages are presented to summarize the trace element concentrations and the metal/calcium atomic ratios of the Pecos Indian bones (Table 4). Adjusted average concentrations of lead, cadmium, silver, and zinc are 44, 27, 63, and 87% of the unadjusted averages, respectively. Adjusted average metal/calcium atomic ratios are 40, 29, 68, and 83% of their unadjusted averages, respectively.

Although the adjusted average skeletal metal levels are the best estimates for ancient North American Pecos Indians, they may also be conservatively high. This qualification is analogous to that detailed in analyses of the previously described ice cores. Lead contamination of the outer core during collection permeated through minute cleavages in the ice and resulted in sequentially decreasing lead concentrations toward the center of the ice core. This indicated that even the lowest lead concentrations at the center of that core might have been contaminated. Therefore, the inner ice core data are considered to be conservatively high estimates of the natural concentrations of lead initially deposited in the ice (49). By analogy, the adjusted average metal levels in inner bone are considered to be conservatively high estimates of the natural levels in ancient North American Pecos Indians.

Discussion

The adjusted estimate of the atomic ratio of lead to calcium in ancient Pecos Indian bones (8.4×10^{-7}) is comparable to the upper range value measured previously (3) in ancient Peruvian bones $(0.9 \text{ to } 7.7 \times 10^{-7})$. These data demonstrate that the average contemporary person may contain up to 500-fold more lead in his skeletal tissues than prehistoric Pecos Indians, who were also exposed to lead concentrations above natural levels. This increase in contemporary individuals is due to anthropogenic perturbations of natural lead cycles, which have greatly increased the bioavailability of this metal. Conclusions on the magnitude of anthropogenic environmental lead contamination based on the present study's adjusted average lead/calcium atomic ratio of

Table 4. Contamination-adjusted mean elemental concentrations and metal/calcium ratios of inner fraction of bone samples of Pecos Indians.^a

Element	Concentration, µg/g dry weight (SD)	п	Atomic ratio, metal/calcium (SD)
Pb	0.65 (0.32)	8 ^b	$\begin{array}{l} 8.4 \ (4.4) \times 10^{-7} \\ 2.6 \ (1.4) \times 10^{-7} \\ 0.83 \ (0.34) \times 10^{-7} \\ 5.4 \ (2.6) \times 10^{-4} \end{array}$
Ag	0.094 (0.044)	12	
Cd	0.032 (0.013)	7	
Zn	130.0 (66.)	13	
Ca	15.0 (1.9%)	14	

"See text for explanation of how values were calculated.

 8.4×10^{-7} must be considered conservatively low compared to the conclusions of Ericson et al. (3), which were based on a corrected lead/calcium atomic ratio in bone and tooth enamel of 0.3×10^{-7} . The discrepancies between these values may be partially due to the presence of diagenetically added contaminant lead in the Pecos Indian bones, which was corrected for differently than in the ancient Peruvian samples, and the inclusion in that study of tooth enamel, which is much less pervious to soil moisture contamination.

The apparent limited production and use of decorated lead glaze paint wares by the Pecos Indians cannot be quantified in these analyses but may partially account for the elevated concentrations of the samples considered contaminated (50). Lead released from ceramic glazes into acidic foods stored in pottery is still among the most frequently cited sources of episodic cases of classic lead toxicity that are attributable to food (51,52). This is also supported by the observation that contemporaneous humans occupationally exposed to lead exhibit increased body lead burdens as some function of exposure (53). A similar approach was used by Aufderheide et al. (42) to predict social correlates based on the skeletal lead content of several colonial American populations. In that study, the investigators observed elevated skeletal lead levels in distinct groups (gender, occupation, and race) of individuals that reflected their increased exposure to lead.

However, it is unlikely that the elevated lead levels of some of the Pecos Indian bones are predominantly due to increased exposure throughout life, rather than contamination postmortem. This view is supported by the absence of any correlates of elevated lead/calcium atomic ratios with the age or gender of the Indians. Exposure to lead via construction of the ceramic wares was generally confined to a relatively few specialists in this trade, and use of the ceramic wares was largely divided along specific classes of gender, age, or tribal rank. Quantifying the contribution of the glaze wares to the body lead burdens of the Pecos Indians could be approached using lead isotopic composition analyses of bone samples, regional lead deposits, and the lead glaze paint wares.

The most conservative unadjusted estimates of the elemental concentrations of silver, cadmium, and zinc in the ancient Pecos Indian bones reveal the likelihood of contamination in some of the samples, which exhibit values for silver $(0.56~\mu g/g)$ and zinc $(450~\mu g/g)$ that are greater than those in modern man $(0.01~to~0.44~\mu g/g)$ and 75 to 170 $\mu g/g$ (14). However, the best estimates of those values (Table 4), using the previously described criteria, indicate prehistoric and modern concentrations of silver and zinc in human bones are essentially the same, while concentrations of cadmium may have increased more than 20-fold to the contemporary human value of $\approx 1.8~\mu g/g$ (14).

A study comparing cadmium body burdens measured in old pathological-anatomical specimens (61 kidneys, 53 livers) from 1897 to 1937 with 1980 modern autopsy samples found that the body burden cadmium concen-

^bOne nondetected value omitted for lead.

tration has increased in modern man by a factor of 4.7 (54). Compiled studies indicate that cadmium increases in the human kidney with time up to 40 years of age (55). No such increase in cadmium with age is apparent in the Pecos Indian bone samples. This is likely due to cadmium accumulating predominantly in kidney and liver tissue and due to the limited and inconclusive number of noncontaminated samples measured. It may also be due to the absence of industrial cadmium during development or the mechanism of cadmium accumulation in living bone. Relating cadmium levels to bone carbon/ nitrogen ratios (protein content) in addition to bone dry weight and calcium content may be more informative in future analyses, since cadmium is predominantly protein-bound in mammals (24,33).

Contrasting processes have been proposed to explain why lead concentrations in some ancient humans are found to be lower than those in bones of modern persons. Some investigators have suggested that biologic lead is leached out from buried bones (56,57) and that this process diminishes lead concentrations with increased burial time. It was concluded, therefore, that lead levels in bones of modern humans are natural (20). A contrasting view suggests that lead in ancient bones corresponds to very low natural levels of biologically accumulated lead, which may be contaminated to some degree by soil moisture lead from natural and anthropogenic sources during burial (3). When these additions are corrected for by comparison with other alkaline earth/calcium ratios, ancient bones are observed to contain extremely low lead/calcium ratios relative to modern humans. We consider the latter viewpoint to be correct and attribute the large relative increase in biologic lead of modern humans to the substantial increase of industrial lead emissions over historical time (21).

In summary, lead levels in ancient Pecos Indian bones, which are comparable to those of ancient Peruvians (3), show discrepancies from levels in modern humans that appear to result from the latter's exposure to anthropogenic sources of lead. Smaller increases in cadmium may be due to either increased exposure to anthropogenic sources of cadmium or an artifact of postmortem bone alteration. In contrast, skeletal levels of zinc and silver do not appear to have measurably increased. Elevated concentrations of lead, cadmium, and zinc in outer bone support the diagenetic addition of those metals to bone during burial. This also supports the earlier findings of Ericson et al. (3) and contradicts the leaching of those elements from bone as proposed by other authors (20).

This work was supported in part by the Milton Fund, Harvard School of Medicine, National Science Foundation (OCE-8612113), National Institutes of Health (ES04291-01), and the University of California Toxic Substances Research and Teaching Program. We acknowledge the assistance of J. B. Cohn, Department of Cell Biology, Johns Hopkins Medical School, and notes of C. B. Ruff, Orthopedic Biomechanics Laboratory, Beth Israel Hospital, Boston, in obtaining Pecos Indian bone samples from the Peabody Museum, Harvard University. We also acknowledge C. C. Patterson, B. Olson, and S. P. DeAtley for earlier comments on this manuscript.

REFERENCES

- 1. Nriagu, J. O. Cupellation: the oldest quantitative chemical process. J. Chem. Educ. 62: 668-674 (1985).
- Patterson, C. C. Natural levels of lead in humans. Carolina Environmental Essay Series III. The Institute for Environmental Studies, University of North Carolina at Chapel Hill, 1982.
- 3. Ericson, J. E., Shirahata, H., and Patterson, C. C. Skeletal concentrations of lead in ancient Peruvians. N. Engl. J. Med. 300; 946-951 (1979).
- 4. Ericson, J. E., Pandolfi, L., and Patterson, C. C. Pyrotechnology of copper extraction: methods of detection and implications. In: Early Pyrotechnology, (S. Wertime and T. Wertime, Eds.), Smithsonian Institute Press, Washington, DC, 1982.
- 5. Ericson, J. E., and Coughlin, E. A. Archaeological toxicology. Ann. N.Y. Acad. Sci. 376; 393-403 (1981).
- Flegal, A. R., and Patterson, C. C. Vertical concentration profiles of Pb in the central Pacific at 15°N and 20°S. Earth Planet Sci. Lett. 64: 19-32 (1983).
- 7. Patterson, C. C., and Settle, D. M. The reduction of order of magnitude errors in lead analyses of biological materials and natural waters by evaluating and controlling the extent and sources of industrial contamination introduced during sample collecting and analysis. In: Accuracy in Trace Analysis: Sampling, Sample Handling, Analysis. National Bureau of Standards Special Publication No. 422 (P. La Fleur, Ed.), National Bureau of Standards, Gaithersburg, MD, 1976, pp. 321-355.
- Sowden, E. M., and Stitch, S. R. Trace elements in human tissues. II. Estimation of the concentrations of stable strontium and barium in human bone. Biochem. J. 67: 103-109 (1957).
- Nusbaum, R. E., Butt, E. M., Gilmour, T. C., and di Dio, S. L. Relation of air pollutants to trace metals in bone. Arch. Environ. Health 10: 227-232 (1965).
- Schroeder, H. A., and Tipton, I. H. The human body burden of lead. Arch. Environ. Health 47: 965-978 (1968).
- 11. Schroeder, H. A., Tipton, I. H., and Nason, A. P. Trace metals in man: strontium and barium. J. Chron. Dis. 25: 491-517 (1972).
- Barry, P. S. I. A comparison of concentrations of lead in human tissues. Br. J. Ind. Med. 32: 119–139 (1975).
- Gross, S. B., Pfitzer, E. A., Yeager, D. W., and Kehoe, R. A. Lead in human tissues. Toxicol. Appl. Pharmacol. 32: 638-651 (1975).
- 14. Iyengar, G., Kollmer, W. E., and Bowen, H. J. M. Elemental Composition of Human Tissues and Body Fluids. Springer-Verlag, Berlin, 1978.
- 15. Nriagu, J. O., and Pacnya, J. M. Worldwide contamination of the air, water and soils with trace metals—quantitative assessment. Nature 333: 134-139 (1988).
- 16. Becker, R. O., Spadaro, J. A., and Berg, E. W. The trace elements of human bone. J. Bone Joint Surg. 50: 326-334 (1968).
- 17. Shapiro, I. M., Needleman, H. L., and Tuncay, O. C. The lead content of human deciduous and permanent teeth. Environ. Res. 5: 467-470 (1972).
- Shapiro, I. M., Mitchell, G., Davidson, I., and Katz, S. H. The lead content of teeth: evidence establishing new minimal levels of exposure in a living preindustrialized human population. Arch. Environ. Health 30: 483-486 (1975).
- 19. Grandjean, P., Nielson, O. V., and Shapiro, I. M. Lead retention in ancient Nubian and contemporary populations. J. Environ. Pathol. Toxicol. 1: 781-787 (1979).
- 20. Jaworowski, Z., Bilkiewicz, J. In: Health Impacts of Different Sources of Energy, IAEA-SM 254-257, International Atomic Energy Agency, Vienna, 1982, pp. 159-167.
- 21. Patterson, C. C., Shirahata, H., and Ericson, J. E. Lead in ancient human bones and its relevance to historical developments of social problems with lead. Sci. Total Environ. 61: 167-200 (1987)
- 22. Ruff, C. B. A reassessment of demographic estimates for Pecos Pueblo. Am. J. Phys. Anthropol. 65: 147-151 (1981).
- Smith, I. C., and Carson, B. L. Trace Elements in the Environ-
- ment, Vol. 2, Silver. Ann Arbor Science, Ann Arbor, MI, 1977. Friberg, L., Elinder, C. G., Kjellstrom, T., and Nordberg, G., Eds. Cadmium and Health: A Toxicological and Epidemiological

- Appraisal, Vol. 1, Exposure, Dose and Metabolism. CRC Press, Boca Raton, FL, 1985.
- Goyer, R. A. Lead. In: Handbook on Toxicity of Inorganic Compounds (H. G. Seiler and H. Sigel, Eds.), Marcel Dekker, New York, 1988, pp. 359-382.
- Elias, R. W., Hirao, Y., and Patterson, C. C. The circumvention of the natural biopurification of calcium along nutrient pathways by atmospheric inputs of industrial lead. Geochim. Cosmochim. Acta 46: 2561-2580 (1982).
- Rosen, J. E., and Pounds, J. G. Quantitative interactions between Pb⁺⁺ and Ca⁺⁺ homeostasis in cultured osteoclastic bone cells. Toxicol. Appl. Pharmacol, 98(3): 530-543 (1989).
- Bratter, P., Gawlik, D., Lausch, J., and Rosick, U. On the distribution of trace elements in the human skeleton. J. Radioanal. Chem. 37: 393-403 (1977).
- Rosen, J. E. Metabolic and cellular effects of lead: a guide to low level lead toxicity in children. In: Dietary and Environmental Lead: Human Health Effects (K. Mahaffey, Ed.), Elsevier, New York, 1985, pp. 157-185.
- Spiro, T. G., Ed. Zinc Enzymes. Metal lons in Biology Series, Vol. 5. John Wiley and Sons, New York, 1983.
- National Research Council. Zinc. Committee on Medical and Biological Effects of Environmental Pollutants, National Academy of Sciences, Washington, DC, 1978.
- Underwood, E. J. Trace Elements in Human and Animal Nutrition, 4th ed. Academic Press, New York, 1977.
- Welinder, H., Skerfving, S., and Henriksson, O. Cadmium metabolism in man. Br. J. Ind. Med. 343: 221-228 (1977).
- Environmental Protection Agency. Health Assessment Document for Cadmium, EPA 600/8-81-023. U. S. EPA, Research Triangle Park, NC, 1982.
- Klaassen, C. D. Biliary excretion of silver in the rat, rabbit, and dog. Toxicol. Appl. Pharmacol. 50: 49-55 (1979).
- Yoshikawa, H., and Ohta, H. Interaction of metals and metallothionein. In: Biological Roles of Metallothionein (E. C. Foulkes, Ed.), Elsevier/North-Holland, Amsterdam, 1982, p. 11.
- Patterson, C. C. Contaminated and natural lead environments of man. Arch. Environ. Health 22: 344-360 (1965).
- Nriagu, J. O. Lead and Lead Poisoning in Antiquity. Wiley Interscience, Toronto, 1983.
- Hooton, E. A. The Indians of Pecos Pueblo: A Study of Their Skeletal Remains. Yale University Press, New Haven, CT, 1980.
- Ruff, C. B. Structural Changes in the Lower Limb Bones with Aging at Pecos Pueblo. Ph.D. dissertation, University of Pennsylvania, Philadelphia, 1981.
- Wittmers, L. E., Jr., Wallgren, A., Alich, A., Aufderheide, A. C., and Rapp, G., Jr. Lead in bone. IV. Distribution of lead in the human skeleton. Arch. Environ. Health 43 (6): 381-391 (1988).

- Aufderheide, A. C., Angel, J. L., Kelly, J. O., Outlaw, E. C., Outlaw, M. A., Rapp, G., and Wittmers, L. E., Jr. Lead in bone. III. Prediction of social correlates from skeletal lead content in four colonial American populations (Catoctin Furnace, College Landing, Governor's Land, and Irene Mound). Am. J. Phys. Anthropol. 66: 353-361 (1985).
- Kidder, A. V. Pecos, New Mexico: archaeological notes. Papers of the R. S. Peabody Foundation for Archaeology, Andover, MA 5: 1-359 (1958).
- Kidder, M. A., and Kidder, A. V. Notes on the pottery of Pecos. A. Anthropol. 19: 325-360 (1917).
- 45. Kidder, A. V. An introduction to the study of southwestern archaeology with a preliminary account of the excavations at Pecos. Papers of the Phillips Academy Southwest Expedition No. 5, Yale University Press, New Haven, CT, 1924.
- Kidder, A. V. The artifacts of Pecos. Papers of the Phillips Academy Southwest Expedition No. 6, Yale University Press, New Haven, CT, 1932.
- Shepard, A. O. Rio Grande glaze-paint pottery, a test of petrographic analysis. In: Ceramics and Man (F. R. Matson, Ed.), Wenner-Gren Foundation, New York, 1965, pp. 62-87.
- Settle, D. M., and Patterson, C. C. Lead in albacore: guide to lead pollution in Americans. Science 207: 1167-1176 (1980).
- Ng, A., and Patterson, C. C. Natural concentrations of lead in ancient Arctic and Antarctic ice. Geochim. Cosmochim. Acta 45: 2109-2121 (1981).
- Jarcho, S. Lead in ancient Pecos Indian bones. A. Antiquity 30: 94-96 (1964).
- Mahaffey, K. R. Environmental exposure to lead. In: The Biogeochemistry of Lead in the Environment (J. O. Nriagu, Ed.), Elsevier/North-Holland, Amsterdam, 1978, pp. 1-39.
- Flegal, A. R., Smith, D. R., and Elias, R. W. Lead contamination in food. In: Food Contamination from Environmental Sources (J. O. Nriagu and M. S. Simmons, Eds.), John Wiley and Sons, New York, 1990, pp. 85~120.
- Ahlgren, L., Haeger-Aronsen, B., Mattsson, S., and Schutz, A. In vivo determination of lead in the skeleton following occupational exposure. Br. J. Ind. Med. 37: 109-113 (1980).
- Drasch, G. A. An increase of cadmium body burdens for this century—an investigation on human tissues. Sci. Total Environ. 26: 111-119 (1983).
- Bowen, H. J. M. Environmental Chemistry of the Elements. Academic Press, London, 1979.
- Grandjean, P., and Holma, B. A history of lead in the Danish population. Environ. Physiol. Biochem. 3: 268-273 (1973).
- Mackie, A., Townshend, A., Waldron, H. A. Lead concentrations in bones from Roman York. J. Arch. Sci. 2: 235-237 (1975).